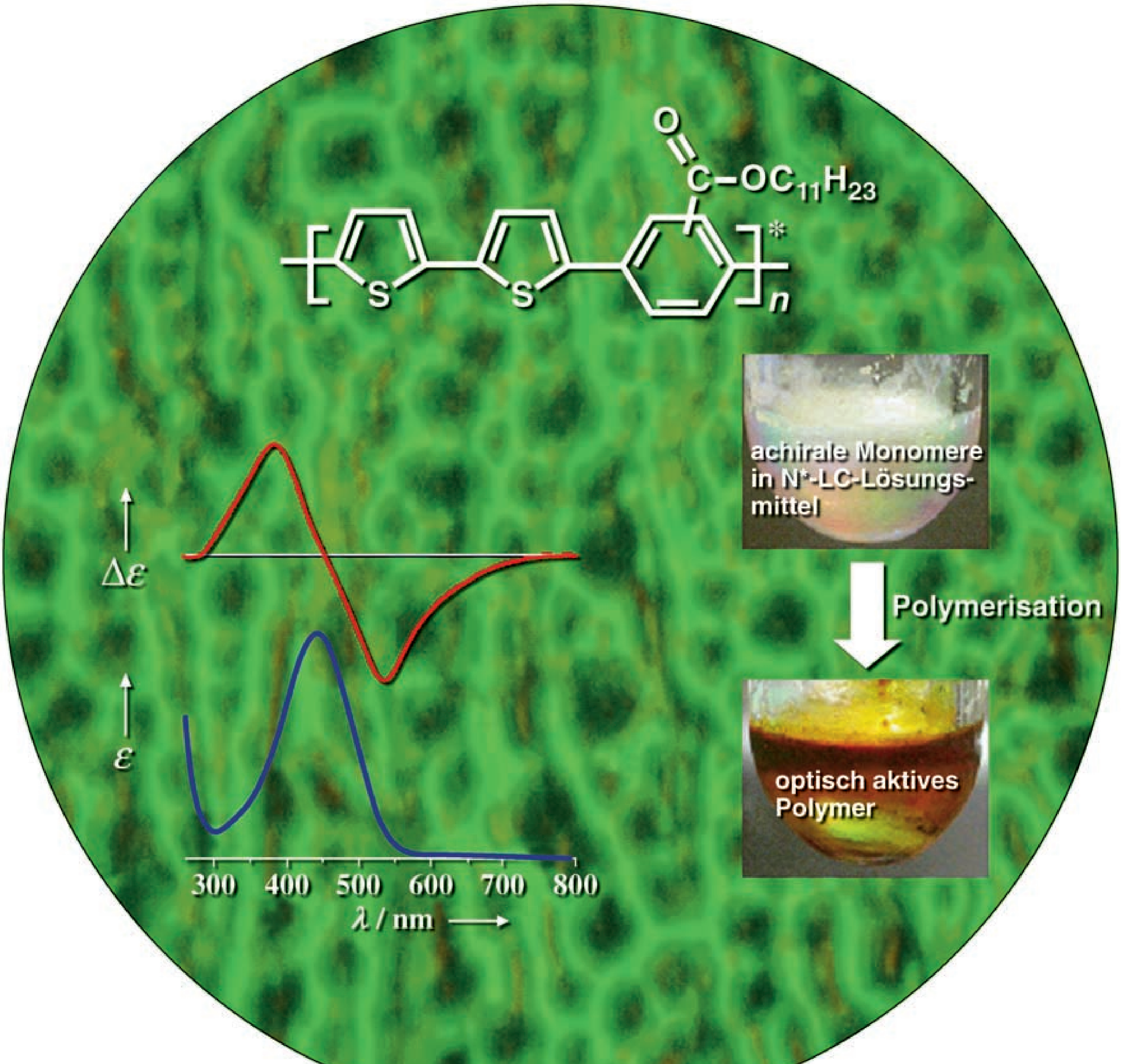
Zuschriften



Chirale Thiophen-Phenylen-Polymere wurden durch eine Stille-Polykondensation in einem chiralen nematischen Flüssigkristall als Solvens aus achiralen Monomeren erhalten. Als Erklärung für die Chiralität des Polymers wird die vom chiralen Medium während der Polymerisation erzeugte Asymmetrie vorgeschlagen. Einzelheiten finden Sie in der Zuschrift von H. Goto und K. Akagi auf den folgenden Seiten.

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Chiral Polymerization

Optically Active Conjugated Polymers Prepared from Achiral Monomers by Polycondensation in a Chiral Nematic Solvent**

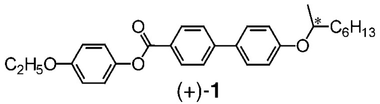
*Hiromasa Goto and Kazuo Akagi**

Asymmetric synthesis is one of the most intriguing research fields in chemistry. Methods for obtaining optically active compounds, such as enantioselective syntheses,[1] asymmetric autocatalytic reactions,[2] asymmetric autoinductions,[3] asymmetric transformations,[4] as well as absolute asymmetric reactions,[5] have been extensively studied. Many approaches to produce stable optically active polymers have also been proposed, such as the introduction of a bulky substituent to a vinyl polymer[6] or an optically active substituent to the polymer side chain,[7] and the induction of chiroptical properties.[8] The synthesis of chiral polymers in an isotropic organic solvent such as tetrahydrofuran (THF), benzene, or diethyl ether requires the use of a chiral monomer or a chiral catalyst.

Liquid crystals are unique in that they exhibit both crystal-like birefringence and fluid behavior. Chiral nematic liquid crystals (N*-LCs) have a quasi-layer structure in which the director of each layer is gradually rotated to produce helicity over several layers. Although liquid crystals exhibit fluid behavior, the crystal-like structural order of N*-LCs can effectively provide chiral order in the propagating step of a polymerization reaction, in contrast to chiral isotropic liquids. However, polymerization reactions performed in liquid-crystal media have received little attention as the liquid-crystalline phase is generally lost upon the addition of a non-liquid-crystal compound.

Helical polyacetylenes with chiroptical properties have been synthesized by using a N*-LC as the reaction medium.[9] The helical polyacetylene prepared in this way exhibited relatively stable chirality as a result of its insolubility and infusibility. In the case of chiral polybithiophene, which was prepared from achiral bithiophene by electrochemical polymerization in a N*-LC electrolyte, the polymer displayed a split Cotton effect in circular dichroism (CD) spectroscopy as well as optically active electrochromism.[10a] N*-LCs are thus considered to provide an effective chiral environment for the control of polycondensation reactions.[10] Herein, we report the use of a nematic liquid crystal as an asymmetric solvent for chiral polymerization and that successful polymerization is dependent on careful consideration of the affinity of the monomer for the N*-LC as well as its solubility therein. We selected a monomer that displays a good affinity for chiral nematic liquid crystals and prepared a stable N*-LC that is suitable for the polycondensation reaction of aromatic compounds and exhibits a chiral nematic phase at around 90 °C as the reaction solvent. The addition of the monomer and the production of the resulting polymer do not affect the liquid crystallinity of the N*-LC reaction medium in this system.

Chiral nematic liquid-crystalline compounds (+)-**1** and (−)-**1**, which comprise a three-ring core with optically active terminal alkyl groups, were prepared as the chiral solvents for the polycondensation reactions. The chiral nematic liquid-crystal phase of these compounds is stable over a wide temperature range and remains stable upon the addition of aromatic compounds such as dibromobenzene and dibromothiophene. The phase-transition behavior of these compounds was determined by differential scanning calorimetry and polarizing optical microscopy (POM) as K 97 (72) N* 135 (133) BP (134) Iso* (K = crystal, N* = chiral nematic, BP = blue phase, Iso* = isotropic; parentheses denote the transition temperature in the cooling process). Both (+)-**1** and (−)-**1** exhibit a frustrated platelet texture of a blue phase and the oily streak texture of a chiral nematic liquid-crystal phase, as observed by POM (see Figure 1 a,b). Generally, high shear stress breaks the helical structure of the N*-LC to result in a nematic phase with no helical structure. However, chiral



(+)-**1**
(−)-**1**

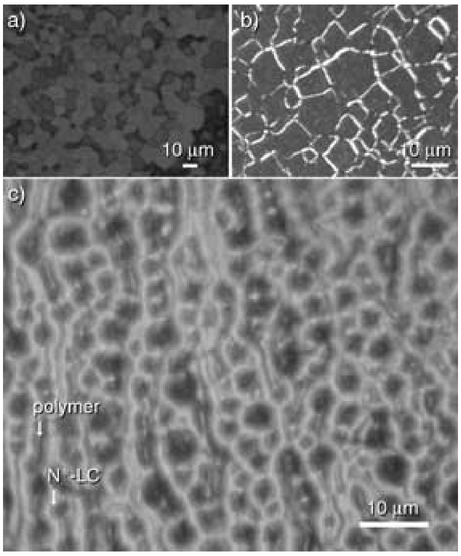


Figure 1. Polarized optical microscopy images: a) Platelet texture of cubic blue phase of (+)-**1** at 134 °C; b) oily streak texture of chiral nematic phase of (+)-**1** at 120 °C; c) presence of polymer mass, (−)-**P2**, and matrix N*-LC (oily streaks) in the reaction mixture at 93 °C after reaction for 24 h.

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[*] Dr. H. Goto, Prof. Dr. K. Akagi
Tsukuba Research Center for Interdisciplinary Materials Science (TIMS)
Institute of Materials Science
University of Tsukuba
Tsukuba, Ibaraki 305-8573 (Japan)
Fax: (+81) 29-855-7440
E-mail: akagi@ims.tsukuba.ac.jp

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nematic liquid crystallinity was confirmed to be maintained under stirring at 80 rpm using a Teflon-coated 1-cm magnetic stirrer bar in a 1.7-cm-diameter Schlenk flask.

Two types of chiral polymer were synthesized in this study: 1) a polymer with chiral substituents prepared in an isotropic organic solvent (THF) and 2) a polymer with no chiral substituents prepared in a chiral nematic liquid crystal as solvent. The syntheses of the polymers through a C–C bond-forming Stille polycondensation reaction are shown in Scheme 1. Brominated chiral benzene derivatives **3** were treated with bis(trimethyltin)-substituted bithiophene derivative **2** in THF under an argon atmosphere in the presence of [Pd(PPh$_3$)$_4$] as catalyst. After 24 h reaction, the mixture was washed with methanol and then acetone to afford the aromatic conjugated polymers with chiral substituents, (+)-**P1** (from **2** and (+)-**3**) and (−)-**P1** (from **2** and (−)-**3**).

Polymerization in the chiral nematic medium was performed by placing 1 g of **1** ((+)-**1** or (−)-**1**) in a small Schlenk flask under argon flow at 93 °C. Iridescence was confirmed due to the selective reflection of light, then **2** (0.1 g, 0.2 mmol) was added and dissolved in the medium. Achiral 2,5-dibromobenzoic acid undecyl ester (**4**; 87 mg, 0.2 mmol) was then added to the mixture and stirred at exactly 80 rpm for 30 min before the addition of a catalytic amount of [Pd(PPh$_3$)$_4$] (3 mg, 0.0026 mmol) to initiate the polycondensation. Stirring was continued at 80 rpm to preserve the chiral nematic liquid crystallinity, and the temperature was maintained at exactly 93 °C during the course of the reaction. Chiral nematic liquid crystallinity was confirmed by monitoring the selective reflection of the mixture during the course of the reaction. Although the transition temperature of the chiral nematic liquid-crystalline phase may be depressed by the introduction of "impurities", namely the monomer, catalyst, or the resulting polymer, this mixture was confirmed to maintain its chiral nematic liquid-crystalline phase at 93 °C. After 24 h reaction, the visible selective reflection of the N*-LC in the reaction flask again confirmed that the chiral nematic liquid-crystalline phase was maintained in the mixture. The mixture in the Schlenk flask also gave rise to a fluorescent emission from the presence of a fluorescent polymeric product in the N*-LC solvent. Figure 1 c shows the POM image of the reaction mixture at 93 °C. Polymer fractions of higher molecular weight which were insoluble in the N*-LC medium were observed as insoluble orange masses surrounded by the oily streak texture of the N*-LC.

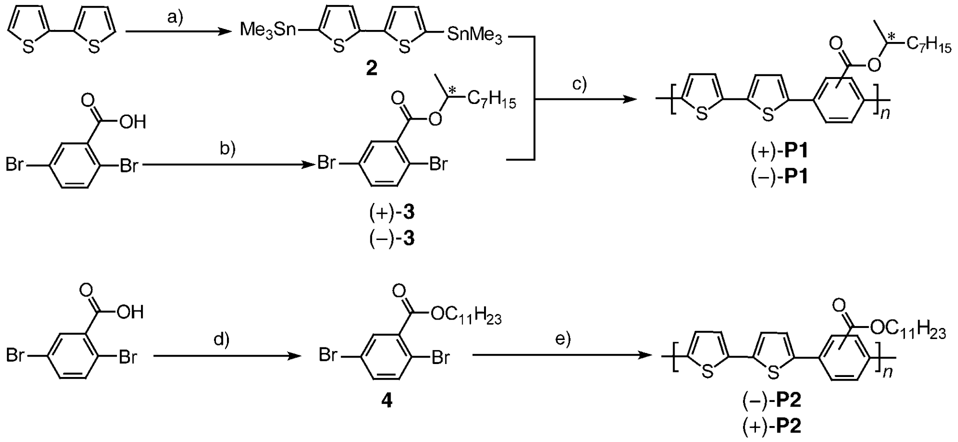
The reaction mixture was allowed to cool to room temperature and then dissolved in a minimal amount of THF, then the solution was poured into a large volume of acetone to dissolve and completely remove **1** (N*-LC) and the fractions of low molecular weight. The product, which was insoluble in acetone, was further washed in acetone and then methanol to leave a red solid that was soluble in THF and CHCl$_3$. The polymers prepared in media (−)-**1** and (+)-**1** are abbreviated (+)-**P2** and (−)-**P2**, respectively. The directions of optical rotation of the polymers were the opposite of those of the N*-LC solvent used.

The results of both sets of polymerization reactions are summarized in Table 1. The number-average molecular weights of (+)-**P1** and (−)-**P1** are 3500 and 3200, respectively, while those of (+)-**P2** and (−)-**P2** are 7000 and 6100, respectively. The quantum efficiency (Φ) of both polymers in CHCl$_3$ was determined as 23 %.

Table 1: Results of polymerization experiments.

Polymer	Monomer	Solvent	Yield [%]	M_n[a]	M_w[b]	MWD[c]	DP[d]	Φ [%][e]
(+)-**P1**	**2**, (+)-**3**	THF	71	3500	4900	1.4	8 (24)	23
(−)-**P1**	**2**, (−)-**3**	THF	75	3200	4700	1.4	8 (24)	23
(+)-**P2**	**2**, **4**	(−)-**1**	86	7000	12 500	1.8	16 (48)	23
(−)-**P2**	**2**, **4**	(+)-**1**	85	6100	9200	1.5	14 (42)	23

[a] Number-average molecular weight evaluated relative to a polystyrene (PS) standard. [b] Molecular weight evaluated relative to PS standard. [c] Molecular weight distribution relative to PS standard. [d] Degree of polymerization relative to PS standard. [e] Fluorescence quantum yield evaluated using quinine sulfate in 1.0 M sulfuric acid as standard.



Scheme 1. Synthetic routes to the polymers. a) *n*BuLi, THF, then Me$_3$SnCl; b) (+)- or (−)-nonanol, DEAD, PPh$_3$, THF; c) [Pd(PPh$_3$)$_4$], THF; d) C$_{11}$H$_{23}$OH, DEAD, PPh$_3$, THF; e) **2**, [Pd(PPh$_3$)$_4$], (+)-**1** or (−)-**1**. DEAD = diethyl azodicarboxylate, * = stereogenic center.

Figure 2 shows the UV/Vis absorption and CD spectra of solutions of the polymers in $CHCl_3$. Polymers (+)-**P1** and (−)-**P1** exhibit maxima (λ_{max}) at 418 nm in the UV/Vis spectrum and CD signals in the region that correspond to the conjugated double bonds of the polymer main chain. They also display mirror-image, exciton-coupled, Davydov-split CD signals at two exciton levels. This splitting is not detected by absorption spectroscopy which indicates an interchain origin of the optical activity and suggests that the polymer has helical interchain organization. Such chiral aggregation of the polymer main chains bears a resemblance to the form of the N*-LC.[7b] Polymer (+)-**P1** displays a positive first and negative second Cotton effect, whereas (−)-**P1** exhibits a negative first and a positive second Cotton effect. This result indicates that the transition moments of (+)-**P1** and (−)-**P1** are clockwise and counterclockwise, respectively.[11] The polymers with chiral substituents have a stable optical activity which is attributable to a stabilization of the chiral structure of the polymer main chain by the ester groups.

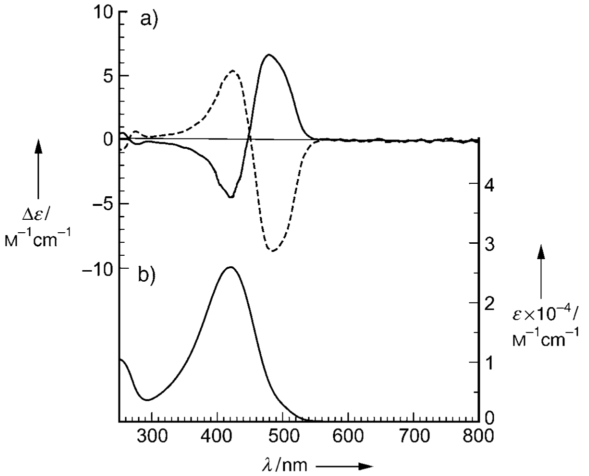


Figure 2. a) Circular dichroism and b) UV/Vis absorption spectra of (+)-**P1** (——) and (−)-**P1** (-----) in $CHCl_3$.

Polymers (+)-**P2** and (−)-**P2**, which were prepared in the N*-LC solvent, display absorbance maxima at 436 nm that tail off toward 800 nm. The CD bands at 380 and 530 nm of solutions of the polymers in $CHCl_3$ are assigned to the bisignate exciton-coupled band associated with the absorption band at 436 nm, and a similar bisignate Cotton effect as seen for **P1** is observed (Figure 3). This result indicates that the transition moments of (+)-**P2** and (−)-**P2** are also oriented clockwise and counterclockwise, respectively. The CD spectrum of (−)-**P2** in THF has almost the same shape as that of (−)-**P2** in chloroform. The expected mirror-image relationship between (+)-**P2** and (−)-**P2** is not caused by the chiral compound that was employed as the solvent in this case because the Cotton effect of **1** is only observed at shorter wavelengths ((+)-**1**: CD ($CHCl_3$): λ_{max} ($\Delta\varepsilon$) = 308 nm ($+0.53\,\text{M}^{-1}\text{cm}^{-1}$); (−)-**1**, CD ($CHCl_3$): λ_{max} ($\Delta\varepsilon$) = 308 nm ($-0.55\,\text{M}^{-1}\text{cm}^{-1}$)).

The polymers **P2** prepared in the N*-LC medium have an optically active structure in isotropic solution. The chiral structure developed during polymerization was preserved even after dissolution and washing, probably as a result of the steric hindrance of the ester groups at the 2-position of the benzene rings which stabilizes the chiral structure of the polymer. To examine the origin of chirality of the polymer, a model compound of low molecular weight was prepared by a Stille reaction. 5-Trimethylstannyl-2,2′-bithiophene[12] and compound **4** were coupled in the same manner as in the preparation of (−)-**P2** to yield the bithiophene–phenylene–bithiophene compound **P3**. This model polymer exhibited no Cotton effect in the CD spectrum which implies that the axial chirality of **P3** was not produced by the N*-LC reaction medium. Thus, the optical activity of **P2** may be derived from chiral aggregation, not axial chirality. However, the optical activity of **P2** may alternatively be caused by a polymer effect such as small changes in one direction in the dihedral angle between repeat monomer units, which would also produce a Cotton effect. Also, high optical rotations in chloroform are obtained for (−)-**P2** ($[\alpha]_D^{20} = -910.1°$) and (+)-**P2** ($[\alpha]_D^{20} = 762.5°$) relative to the lower molecular weight polymers (−)-**P1** ($[\alpha]_D^{20} = -71.8°$) and (+)-**P1** ($[\alpha]_D^{20} = 88.4°$). This result suggests that the polymer effect is important in this system. Although the origin of the Cotton effect cannot be clarified completely on the basis of the results for **P3**, which exhibits neither polymer effects nor aggregation, the experimental results strongly imply that the chirality of **P2** derives from chiral aggregation rather than the helical structure of the main chain (axial chirality). However, in the helical aggregation state of the polymer, several hierarchical levels of chiral structure are plausible, including helical main-chain confor-

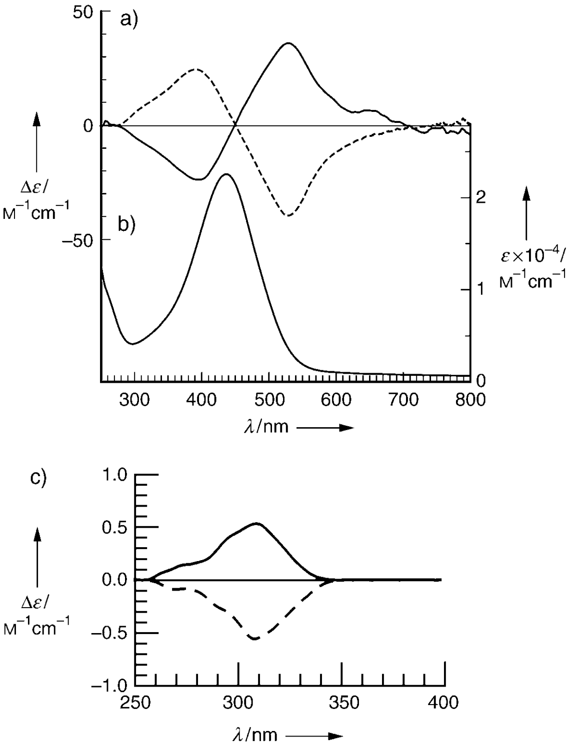


Figure 3. a) CD and b) UV/Vis spectra of (+)-**P2** (——) and (−)-**P2** (-----) in $CHCl_3$. c) CD spectra of N*-LC solvents (+)-**1** (——) and (−)-**1** (-----) measured as solutions in $CHCl_3$.

mations. In this case, the main chain plays a role of a virtual chiral axis.[7b]

Polymers (+)-**P1** and (−)-**P1** exhibit circularly polarized luminescence (CPL) at 500 nm in solution in chloroform, with g_{em} values of -1.1×10^{-3} and $+8.6\times10^{-4}$ at an excitation wavelength $\lambda_{ex}=380$ nm. The degree of circular polarization in the emission is defined by $g_{em}=(I_L-I_R)/[(I_L+I_R)/2]=\Delta I/I=V_{AC}/V_{DC}$, in which I denotes the intensity, subscripts L and R denote left and right, respectively, and V_{DC} and V_{AC} are the values of measured fluorescence and CPL, respectively. Polymers (+)-**P1** and (−)-**P1** display photoluminescence (PL) at 540 nm and CPL centered at 556 nm. Solutions in $CHCl_3$ of (+)-**P2** and (−)-**P2** prepared in the chiral nematic liquid-crystal medium display bisignate and opposite CPL signs ($\lambda_{ex}=380$ nm): $g_{em}=+3.17\times10^{-3}$ (at 620 nm) for (+)-**P2** and $g_{em}=-2.40\times10^{-3}$ (at 620 nm) for (−)-**P2**, as shown in Figure 4. Polymerization under vigorous stirring at 200 rpm produced polymers that exhibit no Cotton effect in CD measurements, which is attributable to the loss of the helical structure of the chiral nematic liquid-crystalline phase as a result of excessive shear stress and growth of the polymer in the nonhelical medium. Green et al. showed that chiral solvents such as (*R*)-2-chlorohexane can transfer chirality to the poly(*n*-hexylisocyanate) main chain of an otherwise achiral polymer.[13] In the present experiments, the chiral structure of the polymer could not be produced when the reaction solvent was in an isotropic or nonhelical state. This is probably a result of the fact that the chirality-inducing property of solvent **1** in the nonhelical state is insufficient to induce chiral aggregation of **P2**, whereas the solvent in a chiral nematic liquid-crystalline mesophase with helical architecture effectively affords a polymer with chiral structure during the polymerization process.

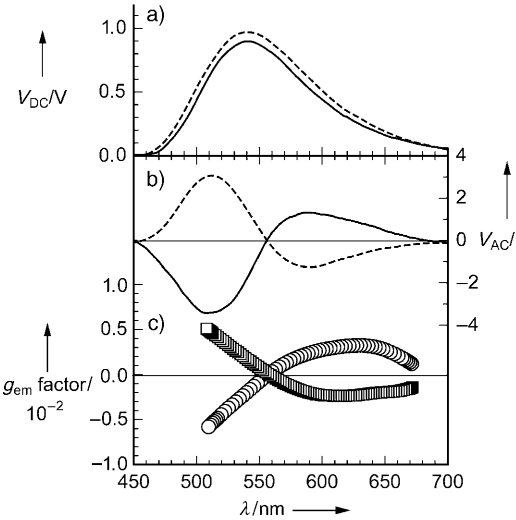


Figure 4. a) PL and b) CPL spectra, and c) g_{em} factors of (+)-**P2** (——, ○) and (−)-**P2** (-----, □) in $CHCl_3$.

Heating of the chiral compounds should result in racemization as a result of the random rotation of polymer main chains and a loss of chiral aggregation. To examine this process, (−)-**P1** and (−)-**P2** were heated in cumene, a solvent of high boiling point. Optical spectra were recorded after the samples had been heated once to 150 °C and then allowed to cool to 25 °C. Heat treatment of (−)-**P1** at 150 °C for 15 min under an argon atmosphere resulted in a weakening, but not complete disappearance, of the Cotton effect. On the other hand, the intensities of the absorption bands of the polymer increased with heating, accompanied by a shift of the maxima to longer wavelengths and an increase in ε values. Figure 5 shows the UV/Vis and CD spectra of (−)-**P2** in cumene under an argon atmosphere before and after heat treatment. Heating the sample at 150 °C for 3 min can be seen to cause a shift of the absorption maxima from $\lambda=458$ to 469 nm and an increase in ε (but decrease in Δε), along with a shift of the CD peaks to longer wavelengths. The heated sample of (−)-**P2** no longer displayed a Cotton effect, although the UV/Vis absorption intensities increased. This result is thought to reflect deaggregation of the polymer, free rotation of the main chain, and a decrease in the average dihedral angle in the main chain during heating. Random rotation of the monomer repeat unit along the polymer main chain as a result of heating is considered to improve the average coplanarity of the polymer measured at 25 °C and increase the effective conjugation length, which leads to an increase in the absorption intensity and a red shift of the absorption peaks. The change in the CD intensities of the annealed polymer in cumene is irreversible.

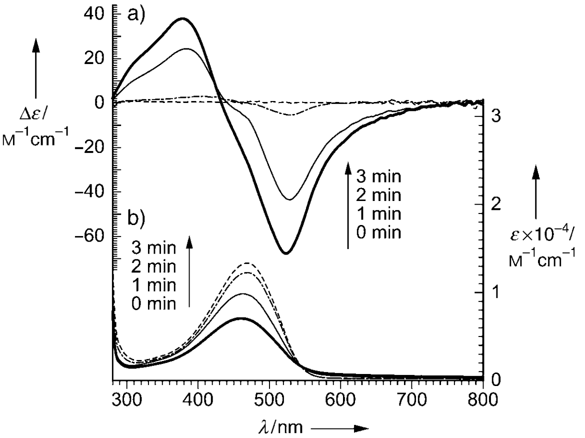


Figure 5. a) CD spectra and b) UV/Vis absorption spectra of (−)-**P2** after heating in cumene for 0, 1, 2, and 3 minutes at 150 °C. These spectra were recorded at 25 °C.

Figure 6 shows the PL and CPL spectra and g_{em} factors for (−)-**P2** before and after heating, with the spectra for (−)-**P2** in $CHCl_3$ shown for reference (thick line). The minima and maxima in the PL spectrum of the polymer in solution in cumene occured at longer wavelengths than in solution in $CHCl_3$, and heating reduced the intensity of the CPL. The emission peaks (minima/maxima) in the CPL spectrum also shifted slightly to longer wavelengths upon heat treatment. The g_{em} factors of (−)-**P2** also decreased upon heating. Heat treatment of (−)-**P2** at 150 °C for 3 min resulted in the loss of the CPL signal, although the polymer exhibited photoluminescence. This CPL result is suggestive of deaggregation of

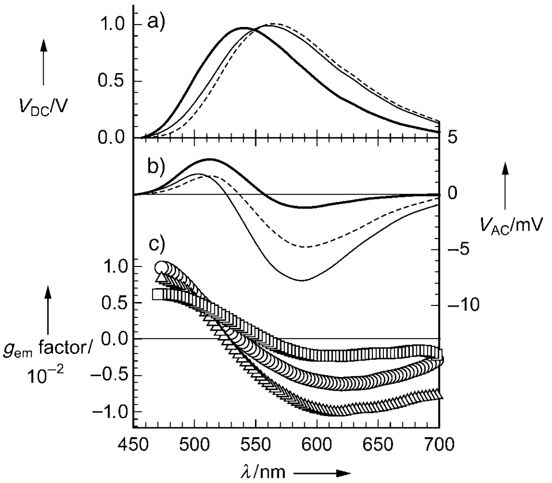


Figure 6. a) PL and b) CPL spectra, and c) g_{em} values of (−)-**P2** in $CHCl_3$ (unheated; bold line, □), in cumene (before heating; ——, △), and in cumene after heating at 150 °C for 1 min (-----, ○). These spectra were obtained at 25 °C.

the polymer and swelling in the solvent upon heating. The chirality of the polymers (+)-**P2** and (−)-**P2**, which contain no chiral substituents, is thus considered to derive from the asymmetry produced by the chiral liquid-crystal medium during polymerization. No chiral molecules reacted with the monomer during the polymerization process, and the N*-LC employed as a solvent functioned only as the reaction medium. In general, the synthesis of chiral polymers requires the introduction of a chiral substituent or the use of a chiral catalyst. The present N*-LC medium thus provides a molecular matrix with central chirality for polymerization, and growth of the polymer in this three-dimensional chiral medium results in the chiral aggregation. The chiral nematic liquid-crystal phase has a chiral helical superstructure with a long helical pitch (> 400 nm), and the small twist angle between quasi-layers of the liquid crystal at the molecular level produces a strong Cotton effect in the CD and CPL spectra of the resultant polymers. The polymerization mechanism has an affinity with the so-called "sergeant-and-soldier" system,[14] as the small asymmetric environment within the quasi-layers of the N*-LC gives consistent optical activity in the resultant polymers. In other words, the "asymmetric field effect" induces the chirality of the polymer aggregation.

In summary, a reaction medium comprised of a chiral nematic liquid crystal leads to chiral aggregation of the conjugated polymer product (as observed by CPL) during the polymerization process, and the aggregation is maintained after visual dissolution of the polymer in chloroform or THF. As enzymes (proteins) form specific stereostructures in which the spacing of the folded protein main chains produce a spatially asymmetric reaction field, the approach proposed in this study may provide a model for biological reactions such as the synthesis of biomolecules in asymmetric environments in living organisms. The results of this study also demonstrate the utility of the chemistry of reaction media.

Experimental Section

All experiments were performed under an argon atmosphere using Schlenk/vacuum line techniques. Tetrahydrofuran (THF), ethanol, acetone, and ether were distilled prior to use. High purity chloroform (Wako) was used without purification for optical measurements of the polymers. ^{1}H NMR spectra were measured in $CDCl_3$ using a Bruker AV-600 FT-NMR spectrometer. Chemical shifts are represented in parts per million downfield from tetramethylsilane (TMS) as an internal standard. Infrared spectra were measured with a JASCO FT-IR 550 spectrometer as KBr disks. Optical absorption spectra were measured in quartz cells at room temperature using a HITACHI U-2000 spectrometer. CD spectra were obtained with a JASCO J-720 spectrometer. PL and CPL measurements of the polymers were performed with a JASCO CPL 200S spectrometer. Phase-transition temperatures were determined using a TA Instrument Q-100 differential scanning calorimeter with a constant heating/cooling rate of 10 °C min^{-1}, and texture observations were made using a Nikon ECLIPS E400 POL polarizing microscope equipped with a Linkam TM 600PM heating/cooling stage. Temperature calibration of the heating stage was carried out by using DSC. The molecular weights of polymers were determined by gel permeation chromatography on a Shodex A-80M column with a JASCO HPLC 870 UV detector using THF, with the instrument calibrated with a polystyrene standard.

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